

AD-A171 156

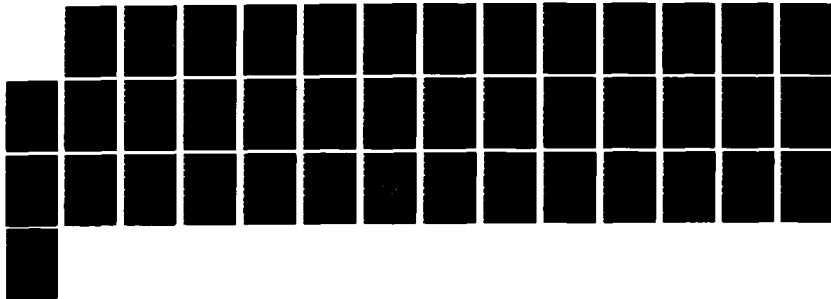
CHEMICALLY RESPONSIVE MICROELECTROCHEMICAL DEVICES  
BASED ON PLATINIZED PO (U) MASSACHUSETTS INST OF TECH  
CAMBRIDGE DEPT OF CHEMISTRY J W THACKERAY ET AL  
22 AUG 86 ONR-RR-9 N00014-84-K-0291

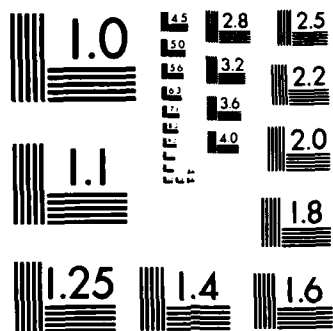
1/1

UNCLASSIFIED

F/G 7/4

NL





MICROCOPY RESOLUTION TEST CHART  
NATIONAL BUREAU OF STANDARDS-1963-A

(2)

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER ONR TR9	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) Chemically Responsive Microelectrochemical Devices Based on Platinized Poly(3-methylthiophene): Variation in Conductivity with Variation in Hydrogen, Oxygen, or pH in Aqueous Solution		5. TYPE OF REPORT & PERIOD COVERED Interim Technical Report
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) J.W. Thackeray and M.S. Wrighton		8. CONTRACT OR GRANT NUMBER(s) N00014-84-K-0291
9. PERFORMING ORGANIZATION NAME AND ADDRESS Department of Chemistry Massachusetts Institute of Technology Cambridge, MA 02139 22007		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS Work Unit # 202-261
11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research Department of the Navy Arlington, VA 22217		12. REPORT DATE August 22, 1986
		13. NUMBER OF PAGES 35
14. MONITORING AGENCY NAME & ADDRESS (If different from Controlling Office)		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report)  Approved for Public release; reproduction is permitted for any purpose of the United States Government; distribution is unlimited.		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report) Distribution of this document is unlimited		
18. SUPPLEMENTARY NOTES Prepared for Publication in <u>Journal of Physical Chemistry</u> B		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number)  Microelectrochemical devices, transistors, electrochemistry		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number)  Attached		

DTIC  
ELECTE  
AUG 27 1986

\$

B

AD-A171 156

DTIC FILE COPY

DD FORM 1473  
1 JAN 73

EDITION OF 1 NOV 65 IS OBSOLETE  
S/N 0102-LF-014-6601

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

### Abstract

Microelectrochemical "transistors" can be prepared by connecting two closely spaced (approximately 1.2 micron) Au microelectrodes (0.1 micron thick x 2.4 micron wide x 50 micron long) with anodically grown poly(3-methylthiophene). The amount of poly(3-methylthiophene) used involves about  $10^{-7}$  to  $10^{-6}$  moles of monomer per  $\text{cm}^2$ . The poly(3-methylthiophene) can be platinized by electrochemical reduction of  $\text{PtCl}_4^{2-}$  at the pair of coated electrodes. The change in conductivity of the poly(3-methylthiophene) with change in redox potential is the basis for amplification of electrical or chemical signals; the conductivity varies by 5 to 6 orders of magnitude upon change in potential from +0.2 (insulating) to +0.7 (conducting) V vs. SCE in aqueous electrolyte. The Pt equilibrates the poly(3-methylthiophene) with the  $\text{O}_2/\text{H}_2\text{O}$  or  $\text{H}_2\text{O}/\text{H}_2$  redox couples. [Poly(3-methylthiophene)/Pt]-based transistors are shown to be viable room temperature sensors for  $\text{O}_2$  and  $\text{H}_2$  in aqueous solution.  $\text{O}_2$  reproducibly turns "on" the device, with 1 atm  $\text{O}_2/0.1 \text{ M HClO}_4/\text{H}_2\text{O}$  showing 0.7 mA  $I_D$  at a  $V_D = 0.2 \text{ V}$ ;  $\text{H}_2$  reproducibly turns "off" the device, with 1 atm  $\text{H}_2/0.1 \text{ M HClO}_4/\text{H}_2\text{O}$  showing less than 20 nA  $I_D$  at a  $V_D = 0.2 \text{ V}$ , where  $V_D$  (drain potential) is the applied potential between the two Au microelectrodes and  $I_D$  (drain current) is the current that passes between the two microelectrodes. The turn "on" with  $\text{O}_2$  is complete within 2 min and the turn "off" with  $\text{H}_2$  is complete within 0.3 min. A platinized microelectrode of a dimension similar to the microelectrochemical transistor shows only 1.0 nA reduction current upon exposure to 1 atm  $\text{O}_2$ ; the current amplification of the transistor is thus a factor greater than  $10^5$ . The transistor device can also reproducibly respond

to pH changes in the pH range of 0 to 12, when there is a constant  $O_2$  concentration; there is a reproducible change in  $I_D$  to alternate flow of a pH 5.5/pH 6.5 stream for over 10 hrs. The device responds to an injection of  $10^{-6}$  l of 0.1 M  $HClO_4$  into an effluent stream of 0.1 M  $NaClO_4$  (flowing at 2 ml per min.) within 4 sec. Study of the resistance properties of the [poly(3-methylthiophene)/Pt] vs. potential reveals that the Pt has little effect on the intrinsic conductivity of poly(3-methylthiophene). Rather, the role of Pt is purely as a catalyst to allow equilibration of  $O_2$  and  $H_2$  with the polymer. The amount of Pt used is approximately  $10^{-7}$  mol/cm<sup>2</sup>, and microscopy shows the Pt to be present as particles of less than 0.1 micron size.



Accession For	
NTIS GRA&I	<input checked="" type="checkbox"/>
DTIC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By	
Distribution/	
Availability	
Dist	
A-1	

DISTRIBUTION LIST

✓ All Reports

Molecular Biology Program, Code 441MB  
Office of Naval Research  
800 N. Quincy Street  
Arlington, VA 22217

✓ Annual, Final and Technical Reports

Defense Technical Information Center (2 copies)  
Building 5, Cameron Station  
Alexandria, VA 22314

Annual and Final Reports Only (one copy each)

Scientific Library  
Naval Biosciences Laboratory  
Naval Supply Center  
Oakland, CA 94625

Commanding Officer  
Naval Medical Research & Development Command  
National Naval Medical Center  
Bethesda, MD 20814

Director  
Infectious Disease Program Center  
Naval Medical Research Institute  
National Naval Medical Center  
Bethesda, MD 20814

Commander  
Chemical and Biological Sciences Division  
Army Research Office  
Research Triangle Park, NC 27709

Commander  
U.S. Army Research and Development Command  
Attn: SGRD-PLA  
Fort Detrick  
Frederick, MD 21701

Commander  
USAMRIID  
Fort Detrick  
Frederick, MD 21701

Commander  
Air Force Office of Scientific Research  
Bolling Air Force Base  
Washington, DC 20332

✓ Administrative Contracting Officer  
Office of Naval Research Laboratory  
(address varies - obtain from Business Office)

✓ Final and Technical Reports Only

Director, Naval Research Laboratory (6 copies)  
Attn: Code 2627  
Washington, DC 20375

[Prepared for publication in the Journal of Physical Chemistry]

CHEMICALLY RESPONSIVE MICROELECTROCHEMICAL DEVICES  
BASED ON PLATINIZED POLY(3-METHYLTHIOPHENE):  
VARIATION IN CONDUCTIVITY WITH VARIATION IN  
HYDROGEN, OXYGEN, OR pH IN AQUEOUS SOLUTION

James W. Thackeray and Mark S. Wrighton<sup>\*</sup>

Department of Chemistry  
Massachusetts Institute of Technology  
Cambridge, Massachusetts 02139

<sup>\*</sup>Address correspondence to this author.

### Abstract

Microelectrochemical "transistors" can be prepared by connecting two closely spaced (approximately 1.2 micron) Au microelectrodes (0.1 micron thick x 2.4 micron wide x 50 micron long) with anodically grown poly(3-methylthiophene). The amount of poly(3-methylthiophene) used involves about  $10^{-7}$  to  $10^{-6}$  moles of monomer per  $\text{cm}^2$ . The poly(3-methylthiophene) can be platinized by electrochemical reduction of  $\text{PtCl}_4^{2-}$  at the pair of coated electrodes. The change in conductivity of the poly(3-methylthiophene) with change in redox potential is the basis for amplification of electrical or chemical signals; the conductivity varies by 5 to 6 orders of magnitude upon change in potential from +0.2 (insulating) to +0.7 (conducting) V vs. SCE in aqueous electrolyte. The Pt equilibrates the poly(3-methylthiophene) with the  $\text{O}_2/\text{H}_2\text{O}$  or  $\text{H}_2\text{O}/\text{H}_2$  redox couples. [Poly(3-methylthiophene)/Pt]-based transistors are shown to be viable room temperature sensors for  $\text{O}_2$  and  $\text{H}_2$  in aqueous solution.  $\text{O}_2$  reproducibly turns "on" the device, with 1 atm  $\text{O}_2/0.1 \text{ M HClO}_4/\text{H}_2\text{O}$  showing 0.7 mA  $I_D$  at a  $V_D = 0.2 \text{ V}$ ;  $\text{H}_2$  reproducibly turns "off" the device, with 1 atm  $\text{H}_2/0.1 \text{ M HClO}_4/\text{H}_2\text{O}$  showing less than 20 nA  $I_D$  at a  $V_D = 0.2 \text{ V}$ , where  $V_D$  (drain potential) is the applied potential between the two Au microelectrodes and  $I_D$  (drain current) is the current that passes between the two microelectrodes. The turn "on" with  $\text{O}_2$  is complete within 2 min and the turn "off" with  $\text{H}_2$  is complete within 0.3 min. A platinized microelectrode of a dimension similar to the microelectrochemical transistor shows only 1.0 nA reduction current upon exposure to 1 atm  $\text{O}_2$ ; the current amplification of the transistor is thus a factor greater than  $10^5$ . The transistor device can also reproducibly respond



to pH changes in the pH range of 0 to 12, when there is a constant  $O_2$  concentration; there is a reproducible change in  $I_D$  to alternate flow of a pH 5.5/pH 6.5 stream for over 10 hrs. The device responds to an injection of  $10^{-6}$  l of 0.1 M  $HClO_4$  into an effluent stream of 0.1 M  $NaClO_4$  (flowing at 2 ml per min.) within 4 sec. Study of the resistance properties of the [poly(3-methylthiophene)/Pt] vs. potential reveals that the Pt has little effect on the intrinsic conductivity of poly(3-methylthiophene). Rather, the role of Pt is purely as a catalyst to allow equilibration of  $O_2$  and  $H_2$  with the polymer. The amount of Pt used is approximately  $10^{-7}$  mol/cm<sup>2</sup>, and microscopy shows the Pt to be present as particles of less than 0.1 micron size.

In this paper we wish to show that metal impregnated conducting polymers can be useful as the active material in microelectrochemical devices that respond to certain chemical changes in aqueous solution. The development of viable chemical microsensors<sup>1,2</sup> is limited by the equilibration of the chemical to be sensed with the microsensor surface. We report here the impregnation of poly(3-methylthiophene) with metallic Pt in order to make the conducting polymer responsive to oxidizing and reducing species,  $O_2$  and  $H_2$ , respectively, in a reversible and reproducible manner at room temperature in aqueous solution, as sketched in Scheme I. As recently described, poly(3-methylthiophene)-based transistors can be used in aqueous solution to reproducibly respond to a redox signal, e.g.  $10^{-16}$  moles of  $IrCl_6^{2-}$  can be detected.<sup>3</sup> In principle, any oxidant capable of oxidizing poly(3-methylthiophene) can be detected. However, only those redox reagents capable of equilibrating with the poly(3-methylthiophene) can be useful in turning the transistor "on" or "off". Since the poly(3-methylthiophene)-based transistor has impressive durability in aqueous solutions, rapid response, and excellent transconductance,<sup>3</sup> this chemically sensitive device is an ideal candidate for microsensor development, provided that it can be made responsive to reagents of interest. Impregnation of the polymer with a noble metal capable of equilibrating with aqueous  $O_2$  and  $H_2$  is our first step in device modification that yields potentially useful functions for the device.

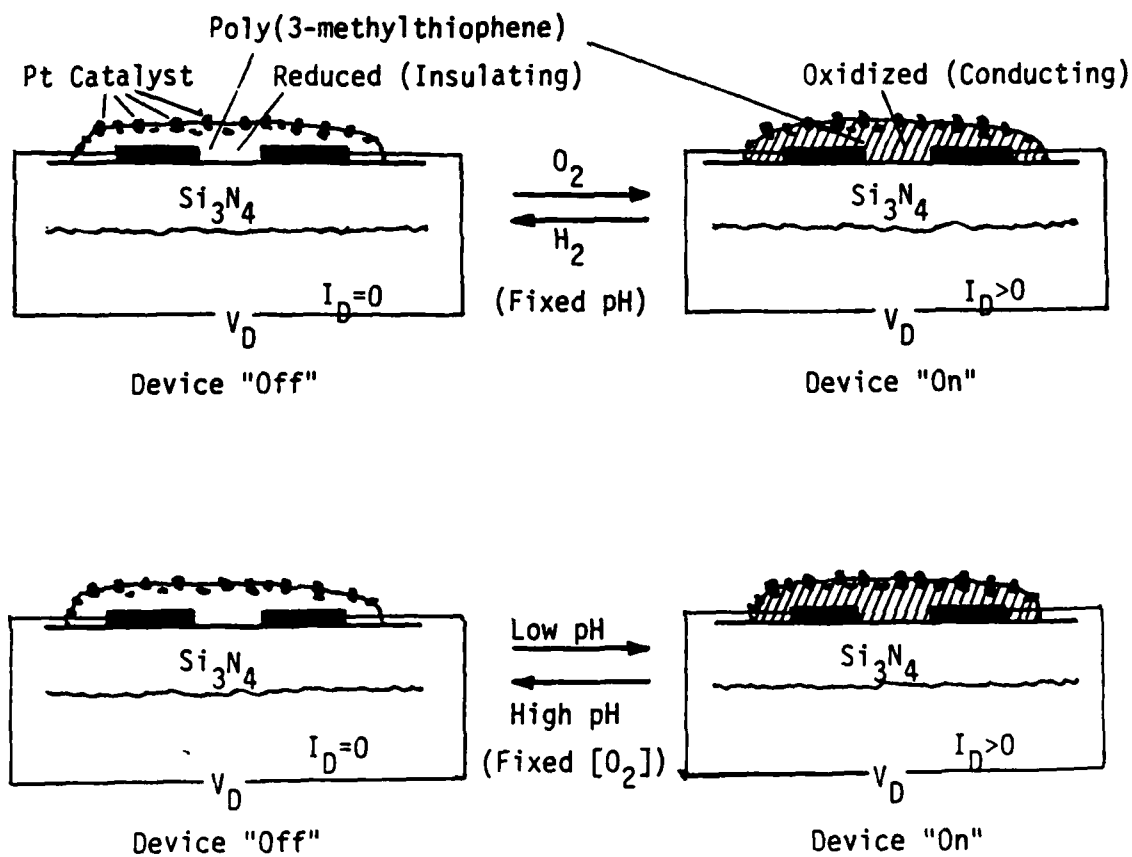
There is considerable precedent for the use of noble metals in redox polymers for the purpose of equilibrating the polymer with the  $H_2O/H_2$  redox couple. The impregnation of viologen-based redox polymers with metallic Pt or Pd has yielded significant advantages in

fabricating useful cathodes and photocathodes for  $H_2$  evolution.<sup>4</sup> Recently, Tourillon and Garnier impregnated poly(3-methylthiophene) with Pt and Ag and showed that such polymers on electrodes exhibit high catalytic activity for  $H_2$  formation, with sustained current densities of  $200 \text{ mA/cm}^2$ .<sup>5</sup> Pt is well known as an active material in electrochemical sensors for  $O_2$ .<sup>6</sup> Pd has been used as the chemically sensitive gate on an  $H_2$ -sensitive CHEMFET which operates well at elevated temperatures.<sup>7</sup> In this paper, we show that the [poly-3-methylthiophene/Pt]-based transistor, Scheme I, responds reversibly and reproducibly to  $O_2$  and  $H_2$  in aqueous electrolyte at room temperature, and, under aerobic conditions, the transistor responds reproducibly to pH from a range of 0 to 12. The key to the response of the microelectrochemical transistor is that the Pt equilibrates the polymer with the redox couple  $O_2/H_2O$  or  $H_2O/H_2$ , resulting in a polymer whose conductivity changes dramatically (up to five orders of magnitude) with variation in the pH (at 1 atm  $O_2$ ) or with change in the atmosphere from  $O_2$  to  $H_2$  at fixed pH.

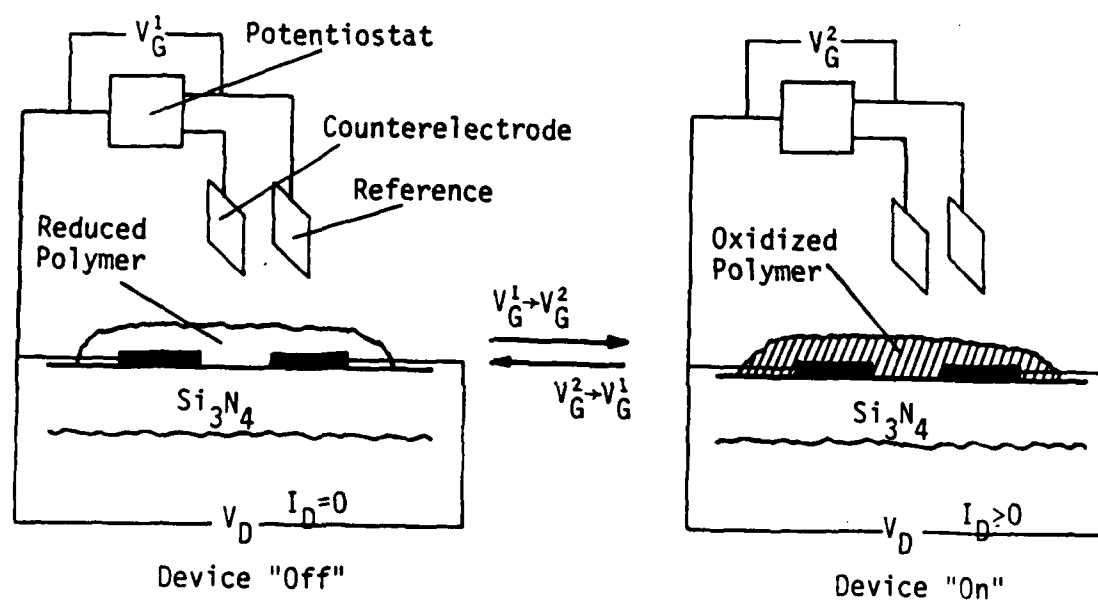
The ability of poly(3-methylthiophene)-based transistors to amplify electrical signals has already been demonstrated by establishing that the average power needed to turn the device on and off, Scheme II, is much smaller than the average power in the drain circuit at frequencies below  $10^3 \text{ Hz}$ .<sup>3b,c</sup> Part of the characterization of the [poly(3-methylthiophene)/Pt]-based transistors includes the demonstration that the Pt incorporated does not substantially alter the performance of the device as an electrical signal amplifier. While there is no presently perceived practical use of such a device, such characterization is essential in establishing the ultimate

performance of sensors based on microelectrochemical transistors. With respect to their electrical properties, poly(3-methylthiophene)- and the [poly(3-methylthiophene)/Pt]-based transistors are essentially the same. The point is that the Pt in the polymer does not appear to affect the conductivity properties of the polymer at a loading where the Pt is an effective catalyst for the equilibration of the polymer with the  $O_2/H_2O$  and  $H_2O/H_2$  redox couples.

Scheme I. Two terminal [poly(3-methylthiophene)/Pt]-based device that can be turned "on" and "off" with  $O_2$  and  $H_2$ , respectively, at fixed pH or with pH variation at fixed  $[O_2]$ .



Scheme II. Representation of a [poly(3-methylthiophene)/Pt]-based transistor that can be turned "on" and "off" by variation in the gate potential,  $V_G$ , from  $V_G^1$  where the polymer is reduced and insulating (device "off",  $I_D = 0$ ) to  $V_G^2$  where the polymer is oxidized and conducting (device "on",  $I_D > 0$ ).



## Experimental Section

Preparation of Microelectrode Arrays. The microelectrode arrays used in this work are those previously described.<sup>8,9</sup> Each chip consists of eight Au microelectrodes with contact leads and pads. The contact pads are symmetrically disposed about the chip, with the array itself occupying  $0.01 \text{ mm}^2$ . The microelectrode arrays are fabricated on 2" diameter single crystal Si wafers on which is grown a 1 micron  $\text{SiO}_2$  layer which is then capped with 0.43 micron  $\text{Si}_3\text{N}_4$  layer. The Au microelectrodes are deposited on top of the  $\text{Si}_3\text{N}_4$  and are thus insulated from the Si. The eight Au microelectrodes are 50 micron x 2.4 micron x 0.1 micron thick and are separated by 1.2 micron. After packaging into electrode assemblies the arrays are typically cleaned with an  $\text{O}_2$  plasma etch (150 W/2 min.) in order to ash residual photoresist. To insure good electrochemical behavior, the arrays are cycled from 0.0 to about -2.0 V vs. SCE in 0.1 M  $\text{K}_2\text{HPO}_4$ , effecting  $\text{H}_2$  evolution at the negative potential. The microelectrodes are then tested by examining their electrochemical behavior in aqueous 0.1 M  $\text{LiCl}/5 \text{ mM Ru}(\text{NH}_3)_6^{3+}$ . A good array shows the same current response for each of the eight microelectrodes: a well-developed current-voltage curve at 50 mV/s for reduction of  $\text{Ru}(\text{NH}_3)_6^{3+}$  characteristic of microelectrodes.<sup>8</sup>

Chemicals. The  $\text{CH}_3\text{CN}$  was HPLC grade and used as obtained from commercial sources. The 3-methylthiophene was obtained commercially and distilled prior to use. The electrolytes were  $[\text{n-Bu}_4\text{N}]\text{ClO}_4$  (Southwestern) for  $\text{CH}_3\text{CN}$  solvent or  $\text{HClO}_4$ ,  $\text{NaClO}_4$ , and/or phosphate buffer for  $\text{H}_2\text{O}$  solvent. All gases were obtained from Matheson Gas

Products, including  $O_2/N_2$  mixtures (1% to 10 ppm). Other gas mixtures were made by utilizing a Matheson Gas Proportioner.

Electrochemical Equipment. The equipment included a PAR Model 173/175 Potentiostat/Programmer for the characterization of macroscopic electrodes and a Pine Instruments RDE 4 Bipotentiostat for the characterization of microelectrodes. A Houston X-Y recorder or an oscilloscope was used to record data using the PAR equipment and a Kipp and Zonen BD 91 X-Y-Y'-T recorder was used for recording characteristics of the microelectrodes. In the two terminal sensing experiments, the counter and reference wires on the RDE 4 were shorted in order to allow the bipotentiostat to supply a floating DC bias,  $V_D$ , between two microelectrodes connected with poly(3-methylthiophene). A DC battery can also be used to provide  $V_D$  and was used in some experiments. The device response to pH,  $O_2$ , and  $H_2$  was monitored by plotting drain current,  $I_D$ , vs. time.

Derivatization of Microelectrodes. Electrochemical oxidation of 3-methylthiophene at Au microelectrodes is accomplished as described in our previous work.<sup>3</sup> Metallic Pt can be deposited in the polymer film by potentiostatting the polymer at -0.3 V vs. SCE in 1 mM  $K_2PtCl_4/H_2O^5$  for a period sufficient to reduce the desired amount of Pt. In  $CH_3CN/0.1 M [n-Bu_4N]ClO_4$ , the cyclic voltammogram of the polymer is the same before and after Pt deposition for Pt deposited at a coverage of about  $10^{-7} \text{ mol/cm}^2$ . In  $H_2O/0.1 M LiClO_4$ , the [poly(3-methylthiophene)/Pt] can not be moved positive of about 0.8 V vs. SCE, due to  $O_2$  evolution. Typically,  $10^{-7} C$  is associated with the interconversion of the insulating and conducting form of the poly(3-methylthiophene) and about  $2 \times 10^{-7} C$  was used to form Pt necessary to



obtain maximum catalytic activity. The typical area of an array covered by a [poly(3-methylthiophene)/Pt]-based transistor is about  $5 \times 10^{-6} \text{ cm}^2$ .

Electrical Characterization of [Poly(3-methylthiophene)/Pt]-Based Transistors. The resistance between a pair of microelectrodes connected with poly(3-methylthiophene) (before and after Pt deposition) was measured by holding one of the two microelectrodes (designated as the "source") at a potential called the gate potential,  $V_G$ , while the potential of the other microelectrode (designated as the "drain") is moved linearly about 20 mV ( $V_D$ ) around  $V_G$ , while monitoring the current,  $I_D$ , that passes between the two microelectrodes.<sup>3a,9</sup> The  $I_D$  vs.  $V_G$  plots in aqueous electrolytes were generated by our previously described methodology.<sup>3,9</sup>

pH Stimulation of a [Poly(3-methylthiophene)/Pt]-based Transistor.

The pH was varied at the surface of a device, Scheme I, by utilization of a 1084b Hewlett-Packard High Pressure Liquid Chromatograph. The HPLC was altered by removing the column. The device was placed directly in the path of the effluent stream, which collected in a glass frit. The solvent collected in the glass frit was saturated with air to provide a fixed  $[O_2]$ . Two methods were used to alter the pH reproducibly. First, we used the gradient programmer to provide alternating compositions of 0.1 M  $NaH_2PO_4$ /0.1 M  $NaClO_4$  (Solvent A) and 0.05 M  $Na_2HPO_4$ /0.1 M  $NaClO_4$  (Solvent B). Second, we injected varying amounts of 0.1 M  $HClO_4$  onto an effluent stream of 0.1 M  $NaClO_4$ . In all such experiments, the flow rate was 2.0 ml/min.

## Results and Discussion

Deposition of Pt Onto Poly(3-methylthiophene). Elemental Pt can be electrochemically deposited onto poly(3-methylthiophene) via reduction of  $\text{PtCl}_4^{2-}$  as described in the Experimental Section. The coverage of Pt was typically about  $10^{-7}$  mol/cm<sup>2</sup> for the experimentation to be described below. A macroscopic Au electrode was first coated with poly(3-methylthiophene) and then with Pt at approximately the same coverage used for the microelectrochemical transistors. Scanning electron microscopy shows that the Pt particles are typically less than 0.1 micron in dimension. Auger spectroscopic investigation of the Au/poly(3-methylthiophene)/Pt electrode shows that the Pt is largely, but not completely confined to the outermost region of the polymer, Figure 1. Such structures have been previously prepared with viologen-based polymers,<sup>4c</sup> but the noble metal can be more cleanly separated from the substrate than demonstrated in Figure 1 for the Au/poly(3-methylthiophene) system. Indeed, it is evident that the Pt can be found throughout the poly(3-methylthiophene). This finding is consistent with the relatively porous, open structure of the poly(3-methylthiophene) compared to the viologen-based systems.<sup>4</sup> The fact that the Pt can be dispersed throughout the poly(3-methylthiophene) represents an advantage in that the polymer/Pt assembly can be regarded as a three dimensional zone of catalytic activity that could yield faster rates of equilibration with sluggish redox couples. The several situations associated with electrocatalysis by polymer coatings on electrodes have been recently discussed.<sup>10</sup>

## Resistance of [Poly(3-methylthiophene)/Pt] as a Function of Potential.

Figure 2 shows the effect of medium, potential, and Pt deposition on

the resistance of poly(3-methylthiophene). First, we note that the resistance varies from  $>10^{10}$  ohms at 0.0 V vs. SCE to  $10^2$  ohms at 0.8 V vs. SCE before and after Pt deposition, in  $\text{CH}_3\text{CN}/0.1 \text{ M } [\text{n-Bu}_4\text{N}]\text{ClO}_4$ . It is interesting that the presence of the metallic Pt has no measurable effect on the potential dependence of the resistance of poly(3-methylthiophene) in  $\text{CH}_3\text{CN}$ . The ability to modulate the conductivity of the polymer is crucial to the sensor function, and it is well-known that metal-filled polymers are good conductors. Thus, it is gratifying to find that the level of Pt required to bring about catalysis (vide infra) of the  $\text{O}_2/\text{H}_2\text{O}$  and  $\text{H}_2\text{O}/\text{H}_2$  redox couples does not lead to potential independent, permanent conductivity of the polymer. In aqueous electrolyte, such as  $\text{H}_2\text{O}/0.1 \text{ M } \text{HClO}_4$ , Pt deposition leads to a small change in the maximum resistance of the poly(3-methylthiophene) in the reduced state;  $8 \times 10^7$  ohms at -0.3 V vs. SCE prior to Pt deposition to  $1 \times 10^7$  ohms at -0.3 V vs. SCE after Pt deposition. Again the small change in the potential dependence of the resistance of poly(3-methylthiophene) in  $\text{H}_2\text{O}$  upon Pt deposition shows that no shorting of the microelectrodes has occurred, and that the primary role of the noble metal is as a catalyst and not in altering the intrinsic potential dependence of the conductivity of poly(3-methylthiophene). We note that the maximum resistance of the poly(3-methylthiophene) in an aqueous electrolyte is less than in  $\text{CH}_3\text{CN}$ , consistent with previous reports of partial doping of poly(3-methylthiophene) in aqueous medium.<sup>11</sup> Further, the deposition of Pt does lower the maximum resistance by about one order of magnitude. Such lowering of the resistance may be due to the formation of  $\text{H}_2$  upon negative potential excursions that can provide a mechanism for

transporting charge from one microelectrode to another. Another possibility is that the aqueous environment brings about a structural change that yields a small amount of conductivity due to the deposited Pt. In any event, the resistance of the poly(3-methylthiophene) can still be varied by about five orders of magnitude upon varying the potential, Figure 2, in an aqueous electrolyte.

Characterization of [Poly(3-methylthiophene)/Pt]-Based Micro-electrochemical Transistors in Aqueous Electrolyte. As expected from data shown in Figure 2, removal of a small amount of electrical charge from the [poly(3-methylthiophene)/Pt] polymer connecting two microelectrodes increases  $I_D$  dramatically, Scheme II and Figure 3. Figure 3 illustrates a typical  $I_D$  vs.  $V_G$  (fixed  $V_D$ ) characteristic in aqueous electrolyte. We see a value for the transconductance,  $g_m$ , of 120 mS/mm of gate width, similar to that previously reported for the poly(3-methylthiophene)-based transistor characterized in  $\text{CH}_3\text{CN}$ .<sup>3a</sup> As reported earlier,<sup>3a</sup> the [poly(3-methylthiophene)/Pt]-based transistor begins to turn "on" at 0.3 V vs. SCE and  $I_D$  achieves a plateau for  $V_G$  more positive than about + 0.8 V vs. SCE. The electrochemical characterization of the transistor shows that chemical oxidants, like  $\text{O}_2$ , and chemical reducing agents, like  $\text{H}_2$ , could turn the device "on" and "off", respectively, if they are capable of equilibrating with the polymer, because  $I_D$  varies strongly in a potential region that is accessible with the  $\text{O}_2/\text{H}_2\text{O}$  redox couple.

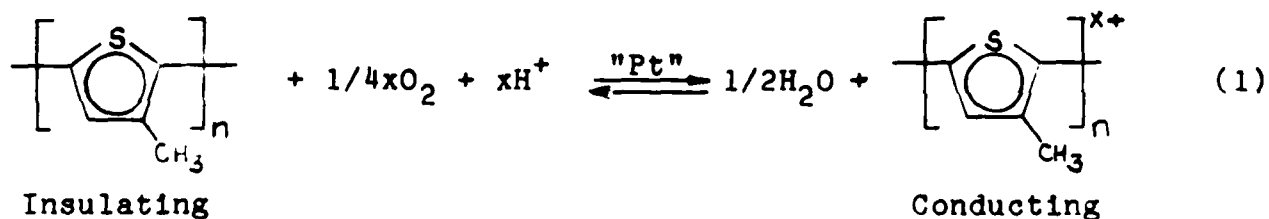
Note that in an electrically-driven characterization, Scheme II, the poly(3-methylthiophene)-based transistor and the [poly(3-methylthiophene)/Pt]-based transistor show no apparent difference in operation. This point is an important one to make in that the ability

to amplify electrical signals with the transistor derived from poly-3-methylthiophene<sup>3b,c</sup> remains intact, while there is an expanded scope of chemicals that can turn on the two terminal device represented by Scheme I, vide infra.

Response of A Two Terminal [Poly(3-methylthiophene)/Pt]-Based Device to O<sub>2</sub> and H<sub>2</sub> Gas. In our earlier work, we showed that a two terminal poly(3-methylthiophene)-based device reproducibly responds to a chemical signal, such as IrCl<sub>6</sub><sup>2-</sup>, to turn on the device because the polymer is oxidized rapidly by the IrCl<sub>6</sub><sup>2-</sup>.<sup>3a</sup> The [poly(3-methylthiophene)/Pt]-based device can be turned on by the O<sub>2</sub>/H<sub>2</sub>O redox couple, E<sup>0</sup>' = 0.99 V vs. SCE at pH = 0, and turned off with the H<sub>2</sub>O/H<sub>2</sub> redox couple, E<sup>0</sup>' = -0.24 V vs. SCE, Scheme I and Figure 4. Figure 4 shows the response of a [poly(3-methylthiophene)/Pt]-based two terminal device to alternate cycling of oxidizing gas, O<sub>2</sub>, and reducing gas, H<sub>2</sub>, in H<sub>2</sub>O/0.1 M HClO<sub>4</sub>. Without Pt, the two terminal device is unresponsive to the gases O<sub>2</sub> and H<sub>2</sub>: the reduced polymer is not oxidized by O<sub>2</sub> to turn on the device and H<sub>2</sub> does not reduce the oxidized polymer to turn off the device. For the Pt-impregnated device exposure to 1 atm O<sub>2</sub> gives I<sub>D</sub> > 0.7 mA at V<sub>D</sub> = 0.2 V. Upon exposure to H<sub>2</sub>, the device is shut "off" to I<sub>D</sub> < 20 nA at V<sub>D</sub> = 0.2 V. The actual response time of the device to the chemical signals varies somewhat from device to device, but the devices all turn on more slowly with O<sub>2</sub> than they can be turned off with H<sub>2</sub>. The faster turn off than turn on is consistent with the fact that the O<sub>2</sub>/H<sub>2</sub>O redox couple has slower kinetics than the H<sub>2</sub>O/H<sub>2</sub> redox couple at Pt.<sup>12</sup> The best devices reach 95% of maximum I<sub>D</sub> in <2 min upon exposure to 1 atm O<sub>2</sub>, and can be turned off to <5% of the maximum I<sub>D</sub> in <0.3 min upon

exposure to 1 atm.  $H_2$ . Rapid, reproducible response of the [poly(3-methylthiophene)/Pt]-based device to a large number of  $O_2/H_2$  cycles over a several hour time period has been demonstrated without variation in the device properties.

While a detailed study has not been made, the data in Figure 4 show that the device turns on to a smaller extent at a partial pressure of  $O_2$  that is significantly less than 1 atm. Figure 5 shows additional data in this regard and also establishes that  $H_2$  is not needed to turn off the device. The value of  $I_D$  for the two terminal device is clearly affected by simply changing the partial pressure of  $O_2$  between 1 and  $10^{-2}$  atm, more or less consistent with the equilibrium indicated in equation (1). Experiments on macroelectrodes



provide additional insight into the catalytic role of Pt in poly(3-methylthiophene). The potential of a [poly(3-methylthiophene)/Pt] macroelectrode is only +0.60 V vs. SCE in 1 atm  $O_2$ /0.1 M  $HClO_4/H_2O$ , and a potential of -0.30 V vs. SCE in 1 atm  $H_2$ /0.1 M  $HClO_4/H_2O$ . The potential difference, 0.9 V, is smaller than that expected ideally, 1.23 V. All of the voltage loss, 0.33 V, is associated with the  $O_2/H_2O$  couple ( $E^0 = 0.93$  V vs. SCE, at pH 1.0). However, the voltage loss is also seen at similarly platinized Pt and platinized Au macroelectrodes. Therefore, the catalytic Pt in poly(3-methylthiophene) appears to be as effective as Pt itself, and the non-

ideal behavior of Pt in equilibrating with  $O_2$  explains the voltage loss.<sup>12</sup> The inability to achieve the  $O_2/H_2O$  potential is likely associated with achieving a mixed potential arising from the  $O_2/H_2O_2$  redox couple,  $E^{\circ'} = +0.44$  V vs. SCE at pH = 0. Incidentally, small amounts of  $H_2O_2$  in aqueous electrolyte do not turn on a non-platinized poly(3-methylthiophene)-based two terminal device, whereas the platinized device is responsive.

The two terminal device illustrated in Scheme I obviously turns on with  $O_2$  in  $HClO_4$ . The device can also be turned on in the presence of other acids including pH = 1 solutions of  $HNO_3$ ,  $HF_4$ , and  $H_2SO_4$ . For a given device there is about a factor of two lower value of  $I_D$  at 1 atm  $O_2$  for the  $H_2SO_4$ , but the other acids give the same maximum value of  $I_D$  within experimental error. It is known that there is variation in the conductivity of conducting polymers depending on the charge compensating anion, but it has been suggested that poly(3-methylthiophene) is somewhat less sensitive to anion than other polymers, e.g. polypyrrole,<sup>13</sup> because of its more open structure.<sup>11</sup>

It is possible to establish that a kind of amplification of the chemical signal can be realized with a [poly(3-methylthiophene)/Pt] device. A pair of "naked" Au microelectrodes with the same amount of Pt deposited on their surface can be held at 0.0 V vs. SCE and the reduction current for the reduction of  $O_2$  in  $H_2O$  can be monitored. For the pair of "naked" microelectrodes, the largest reduction current was 1.0 nA, in a situation where  $I_D > 0.7$  mA is found upon turn on with  $O_2$  of a two terminal [poly(3-methylthiophene)/Pt] device. The ratio of  $I_D$  to the reduction current at the pair of naked microelectrodes is thus greater than  $7 \times 10^5 : 1$ . The point is that

the charge needed to turn on the transistor results in a large flow of charge in the drain circuit of the device and represents a larger signal than can be achieved by a conventional amperometric detection of the  $O_2$  in solution. Thus, smaller  $O_2$  signals should be detectable at the transistor device.

The "naked" microelectrodes for amperometric detection showed switching times similar to those for  $O_2/H_2$  cycling as found for the [poly(3-methylthiophene)/Pt] transistor; i.e. 2 min to show 95% of maximum reduction current for  $O_2$ , and 0.3 min to show 95% of maximum oxidation current for  $H_2$ . The similar turn "on" and turn "off" times for the platinized microelectrodes and the [poly(3-methylthiophene)/Pt]-based device indicate that the Pt on the polymer is as effective catalytically as on a "naked" Au surface. However, it should be noted that the surface area associated with the polymer supported Pt may be much greater than for the smooth Au surface. In previous work it was found that the catalytic activity per unit mass of noble metal is lower on the viologen-based polymers than on the surface of solid electrode materials.<sup>14</sup>

Response of Two Terminal [Poly(3-methylthiophene)/Pt]-Based Devices to Variation of pH. Figure 6 shows  $I_D$  of a two terminal [poly(3-methylthiophene)/Pt] device vs. pH for an  $O_2$ -saturated aqueous electrolyte. The oxidizing power of the  $O_2/H_2O$  couple is reduced by 60 mV/pH upon moving to more basic conditions. Thus, the drain current is reduced dramatically in shifting from pH 1 to pH 12.0. Above pH 12, the device shows no response to  $O_2$ -saturated solutions. At pH 12 (0.1 M  $Na_3PO_4$ /0.1 M  $NaClO_4$ ), we measure a lower limit variation of  $I_D$  of 50 nA upon  $O_2/H_2$  cycling. Operationally, the



device shows the largest, most easily detectable response in acidic solutions, but reproducible response can also be achieved in neutral and basic solutions. It is important to note that  $I_D$  does not vary linearly with pH, Figure 6, as expected from the transistor characteristic shown in Figure 2. Variation in pH at fixed  $[O_2]$  is expected to result in a 59 mV/pH shift in the potential, and this is approximately the case. However, as noted above the Pt catalyst does not bring the polymer to the standard potential for the  $O_2/H_2O$  redox couple. Accordingly, the characteristic in Figure 2 does not predict the pH response shown in Figure 6. The data in Figure 2 would lead to the expectation that the two terminal device would show the maximum slope in the  $I_D$  vs. pH plot at a pH of about 7 where  $E^0(O_2/H_2O) = +0.57$  V vs. SCE. In fact, the maximum slope in the  $I_D$  vs. pH plot, Figure 6, occurs near pH 4, because the Pt does not bring the polymer to the reversible  $O_2/H_2O$  potential. Thus, as for response to  $O_2$  at fixed pH, the response of the two terminal device in Scheme I to pH variation at fixed  $[O_2]$  is not that predicted from the electrical characteristic of the transistor in Scheme II, because the Pt is not an ideal catalyst for the  $O_2/H_2O$  redox couple.

The two terminal [poly(3-methylthiophene)/Pt] device shows reproducible response to pH variation at fixed  $[O_2]$  for a long period of time. Figure 7 shows  $I_D$  vs. time while changing the pH repetitively between 5.5 and 6.5 at  $V_D = 0.2$  V. The pH change was accomplished by using the gradient programmer of an HPLC, where solvent A contained pH 5.5, 0.1 M  $NaH_2PO_4$ /0.1 M  $NaClO_4$ , and solvent B contained pH 8.6, 0.05 M  $Na_2HPO_4$ /0.1 M  $NaClO_4$ . By programming the

HPLC, a reproducible pH variation could be delivered to the two terminal device for "10 h.

Data in Figure 7 demonstrate drift-free and constant response to pH variation for the entire experiment. It should be emphasized that the experiment does not demonstrate the lifetime of useful function. Rather, the data shown establish that the lifetime is at least 10 h. In fact, the device used to collect the data in Figure 7 also responded, drift-free, for another 6 h to a pH variation between 5.5 and 3.5 with a reversible, reproducible change in  $I_D$  of 3.0 microamps (larger  $I_D$  at lower pH). An impressive feature of the long term experiments involving pH variation at fixed  $[O_2]$  is that the devices can operate with negligible drift. This is surprising because it is well known that Pt is easily poisoned; under the carefully controlled conditions used in the experimentation the overall function of the device is constant. This information does not prove that practical applications will emerge, but the data do show that the activity of the catalyst and the properties of the conducting polymer are intrinsically sufficiently persistent to achieve useful functions. Considering that the Pt probably leads to the creation of some  $H_2O_2$ , vide supra, the long term constant operation in experiments like that summarized by Figure 7 suggests that the [poly(3-methylthiophene)/Pt] system is oxidatively durable. One final point should be made concerning durability. In an experiment like that in Figure 7 there is a constant current passing from one microelectrode to another and in one direction. During the experiment  $>10^5$  C/cm<sup>2</sup> pass through each microelectrode/polymer interface at a current density of  $>3$  A/cm<sup>2</sup>. In practical applications there is probably merit in considering the use

of periodic variation in the sign of  $V_D$ . At least this would minimize the migration of the Pt catalyst. In the experiments carried out thus far we have not found problems from catalyst migration, but it is a problem that is likely to be encountered in long term operation of such devices.

Figure 7 does not establish the response time of the device to pH change. In Figure 7 the response of the device follows the variation of pH. A rapid change in pH could be delivered by direct injection of a pulse of 0.1 M  $\text{HClO}_4$  into an effluent stream of 0.1 M  $\text{NaClO}_4$ . The detection of such a pH "jump" is illustrated in Figure 8. There is a fast, reproducible response to a change in pH when 1.0 microliter of 0.1 M  $\text{HClO}_4$  ( $1 \times 10^{-7}$  moles  $\text{H}^+$ ) is injected. We see a change in  $I_D$  of 1.0 microamp at  $V_D = 0.1$  V. Again, the change in  $I_D$  is reproducible over many injections, and the speed of response is constant. The turn "on" time is  $<4$  s.

### Conclusions

The characterization of the [poly(3-methylthiophene)/Pt]-based devices sketched in Schemes I and II show that the Pt can be deposited in an amount that will allow the polymer to be equilibrated with the  $O_2/H_2O$  and  $H_2O/H_2$  redox couples without significantly altering the essential potential dependence of the conductivity of the polymer. Thus the [poly(3-methylthiophene)/Pt] composite material is chemically sensitive in a way that allows the demonstration of microelectrochemical devices responsive to  $H_2$  and  $O_2$  at fixed pH and to pH at fixed  $[O_2]$ . The Pt catalyst is nearly ideal for the  $H_2O/H_2$  redox couple in that rapid response can be achieved and the polymer can be equilibrated to the standard potential. The Pt catalyst is less effective for the  $O_2/H_2O$  redox couple; the response is slower and the standard potential is not achieved with the Pt-impregnated polymer. The catalytic activity of Pt in the poly(3-methylthiophene) parallels its behavior in other situations.<sup>12</sup>

The interesting property of the [poly(3-methylthiophene)/Pt] material is that the conductivity can be varied by five orders of magnitude in acid solution by changing the atmosphere from  $H_2$  to  $O_2$ . This suggests that there may be useful applications as a sensor, but there are at least two problems that should be mentioned. First, the two terminal device is a "floating" device without a reference electrode and operates as a system that responds to the potential of the medium at a rate that is dependent on having active catalyst. The catalyst is a noble metal known to be easily deactivated. Second, the conductivity of the polymer is likely to be somewhat electrolyte dependent, for a given potential. More elaborate characterization of

the electrolyte dependence is required to assess whether the device is practical. As a pH sensor at fixed  $[O_2]$  the device also has some possible shortcomings related to the issues mentioned above. However, the demonstration of reproducible response under laboratory conditions, Figure 7, provides evidence that there is not an intrinsic materials limitation that rules out useful devices.

It should be emphasized that the electrical characteristics of the device in Scheme II are essentially the same with and without the Pt in the polymer. The point is that the data in Figure 3 are the same as would be obtained without the Pt catalyst. There are electroactive materials that have an intrinsic pH dependence that can be useful in demonstrating devices that are responsive to pH variation where the device is operated as in an ISFET,<sup>1</sup> where  $V_G$  and  $V_D$  are fixed. In this regard research in the Wrighton group<sup>15</sup> has been directed toward characterization of microelectrochemical transistors based on a quinone-containing polymer,<sup>16,17</sup> polyvinylpyridine,<sup>18</sup> or metal oxides.<sup>19,20</sup> Unlike the poly(3-methylthiophene) these materials have an intrinsic pH dependence that yields pH-dependent transistor characteristics. However, a significant disadvantage of such materials compared to the [poly(3-methylthiophene)/Pt] composite is that the devices have maximum value of  $I_D$  that is substantially lower. Research in the Wrighton group is now directed toward the synthesis of intrinsically chemically sensitive redox polymers that have high maximum conductivity.

Acknowledgments. We thank the Office of Naval Research and the Defense Advanced Research Projects Agency for partial support of this research.

### References

1. Janata, J.; Huber, R.J. "Solid State Chemical Sensors", Academic Press, Orlando, Florida, 1985.
2. (a) Wohltjen, H. Anal. Chem., 1984, 56, 87A.; (b) Dessy, R.E. Anal. Chem., 1985, 57, 1188A.
3. (a) Thackeray, J.W.; White, H.S.; Wrighton, M.S. J. Phys. Chem., 1985, 89, 5133; (b) Lofton, E. P.; Thackeray, J. W.; Wrighton, M. S., submitted; (c) Thackeray, J. W. Ph.D. Thesis, M. I. T., 1985.
4. (a) Bookbinder, D.C.; Bruce, J.A.; Dominey, R.N.; Lewis, N.S.; Wrighton, M.S. Proc. Natl. Acad. Sci., USA, 1980, 77, 6280; (b) Dominey, R.N.; Lewis, N.S.; Bruce, J.A.; Bookbinder, D.C.; Wrighton, M.S. J. Am. Chem. Soc., 1982, 104, 467; (c) Bruce, J.A.; Murahashi, T.; Wrighton, M.S. J. Am. Chem. Soc., 1982, 104, 1552.
5. Tourillon, G.; Garnier, F. J. Phys. Chem., 1984, 88, 5281.
6. Clark, L.C. Jr. Trans. Am. Soc. Artif. Intern. Organs, 1956, 2, 41.
7. Lundstrom, I.; Shivaraman, M.S.; Svensson, C. J. Appl. Phys., 1975, 46, 3876.

8. (a) Kittlesen, G.P., White, H.S.; Wrighton, M.S. J. Am. Chem. Soc., 1985, 107, 7373; (b) Kittlesen, G.P.; Wrighton, M.S. J. Mol. Electronics, 1986, 2, 23.
9. (a) White, H.S.; Kittlesen, G.P.; Wrighton, M.S. J. Am. Chem. Soc., 1984, 106, 5375; (b) Kittlesen, G.P.; White, H.S.; Wrighton, M.S. J. Am. Chem. Soc., 1984, 106, 7389; (c) Paul, E.W.; Ricco, A.J.; Wrighton, M.S. J. Phys. Chem., 1985, 89, 1441.
10. (a) Andrieux, C. P.; Dumas-Bouchiat, J. M.; Saveant, J. M. J. Electroanal. Chem., 1982, 131, 1; (b) Andrieux, C. P.; Saveant, J. M. J. Electroanal. Chem., 1982, 134, 163; (c) Anson, F. C.; Saveant, J. M.; Shigahara, K. J. Phys. Chem., 1983, 87, 214.
11. Tourillon, G.; Garnier, F. J. Electroanal. Chem., 1984, 161, 407.
12. (a) Hoare, J.P. "The Electrochemistry of Oxygen"; Interscience, New York, 1968; (b) Hoare, J.P. J. Electrochem. Soc., 1965, 112, 849; (c) Hoare, J.P. J. Electrochem. Soc., 1965, 112, 602; (d) Hoare, J.P. J. Electrochem. Soc., 1962, 109, 858.
13. (a) Waltman, R.J.; Bargon, J.; Diaz, A.F. J. Phys. Chem., 1983, 87, 1459; (b) Diaz, A. Chem. Script., 1981, 17, 145.
14. Harrison, D. J.; Wrighton, M. S. J. Phys. Chem., 1984, 88, 3932.

15. Wrighton, M. S.; Thackeray, J. W.; Natan, M. J.; Smith, D. K.; Lane, G. A.; Belanger, D. Philo. Trans. Roy. Soc. Ser. B, in press.
16. Smith, D. K.; Lane, G. A.; Wrighton, M. S. J. Am. Chem. Soc., 1986, 108, 3522.
17. Smith, D. K.; Lane, G. A.; Wrighton, M. S., to be submitted.
18. Belanger, D.; Wrighton, M. S., to be submitted.
19. Natan, M. J.; Mallouk, T. E.; Wrighton, M. S. J. Phys. Chem., submitted.
20. Natan, M. J.; Belanger, D.; Carpenter, M. K.; Wrighton, M. S., to be submitted.



### Figure Captions

Figure 1. Auger signal intensities as a function of Ar ion sputtering time for a macroscopic Au electrode first modified with poly(3-methylthiophene) and then with elemental Pt as outlined in the Experimental Section.

Figure 2. Resistance between two poly(3-methylthiophene)-connected microelectrodes as a function of  $V_G$  in (A)  $\text{CH}_3\text{CN}/0.1 \text{ M } [\text{n-Bu}_4\text{N}]\text{ClO}_4$ , before and after Pt deposition and in (B)  $\text{H}_2\text{O}/0.1 \text{ M } \text{HClO}_4$  before Pt deposition and in (C)  $\text{H}_2\text{O}/0.1 \text{ M } \text{HClO}_4$  after Pt deposition.

Figure 3. Drain Current,  $I_D$ , vs. gate potential,  $V_G$ , at fixed  $V_D = 0.200 \text{ V}$ , for a [poly(3-methylthiophene)/Pt]-based transistor in  $\text{H}_2\text{O}/0.1 \text{ M } \text{HClO}_4$  as in Scheme II.

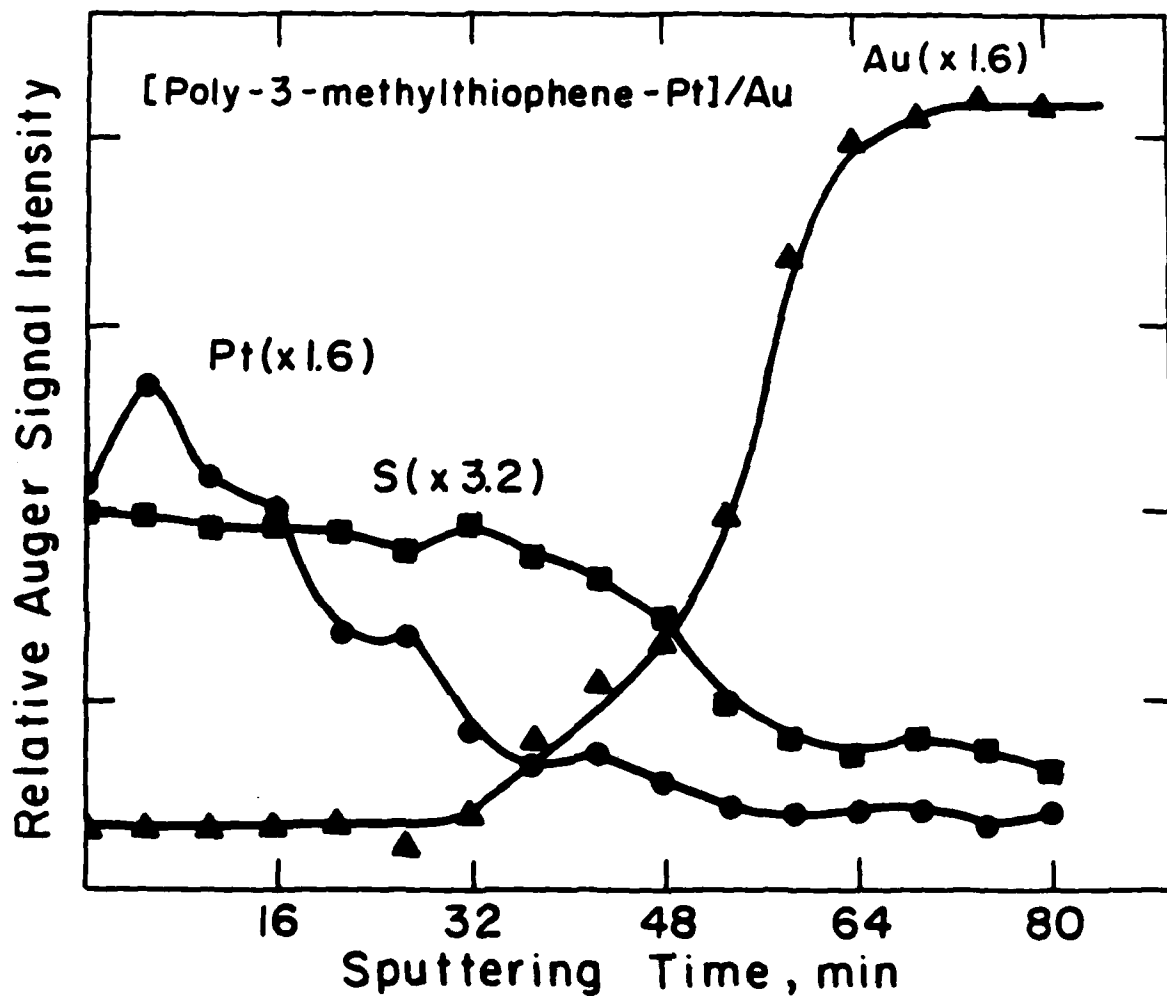
Figure 4.  $I_D$  vs. time for a two terminal [poly(3-methylthiophene)/Pt]-based device, Scheme I, upon exposure to  $\text{O}_2$  and  $\text{H}_2$  gas in  $0.1 \text{ M } \text{HClO}_4/\text{H}_2\text{O}$ . In all cases the total pressure is 1 atm, with  $\text{N}_2$  as a diluent for the  $10^{-2}$  atm  $\text{O}_2$  signal.

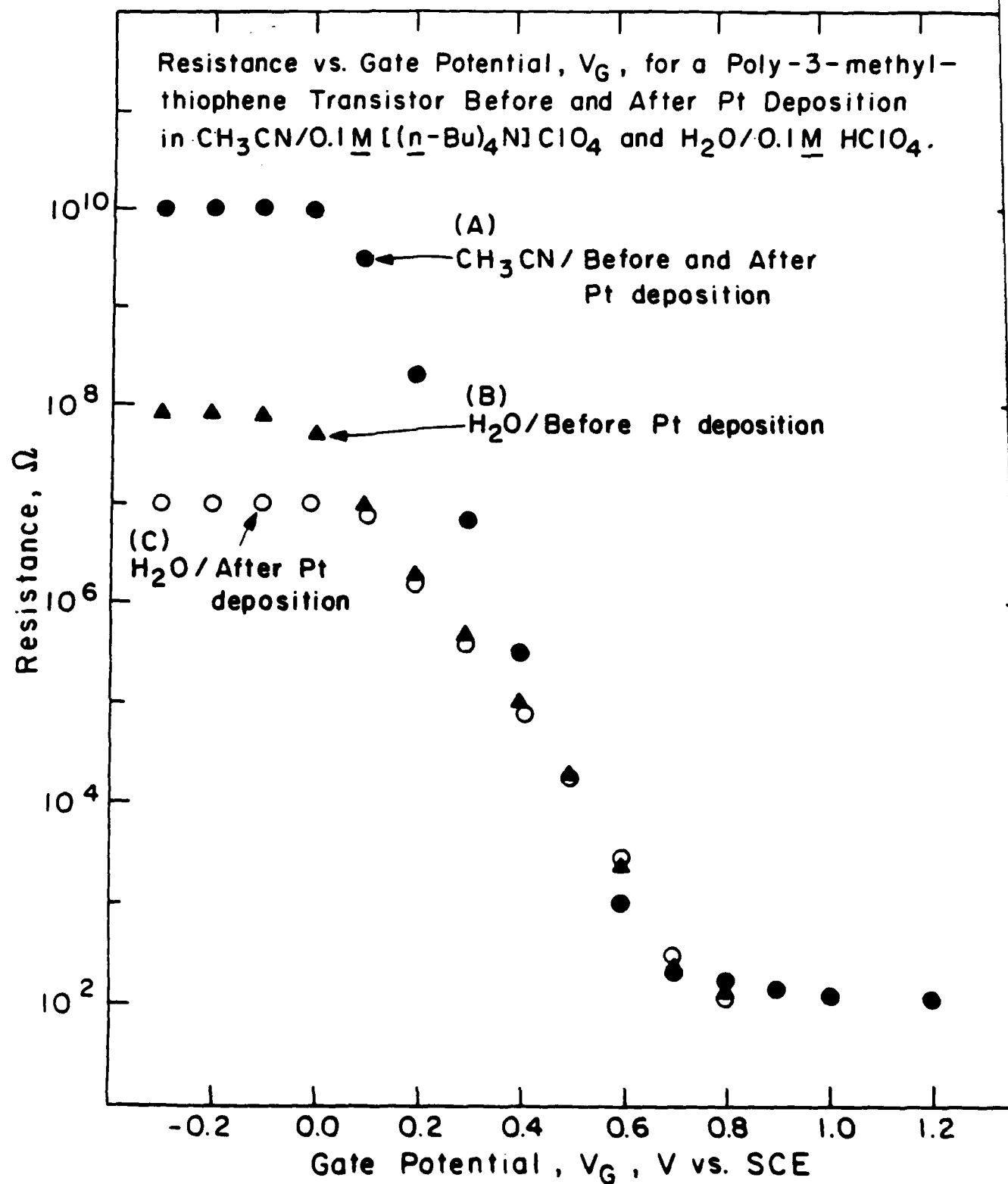
Figure 5. Response of a two terminal [poly(3-methylthiophene)/Pt]-based device to variation in  $\text{O}_2$  partial pressure (total pressure 1 atm) to show that the device does not require  $\text{H}_2$  to be turned off, consistent with the equilibrium represented by equation (1).

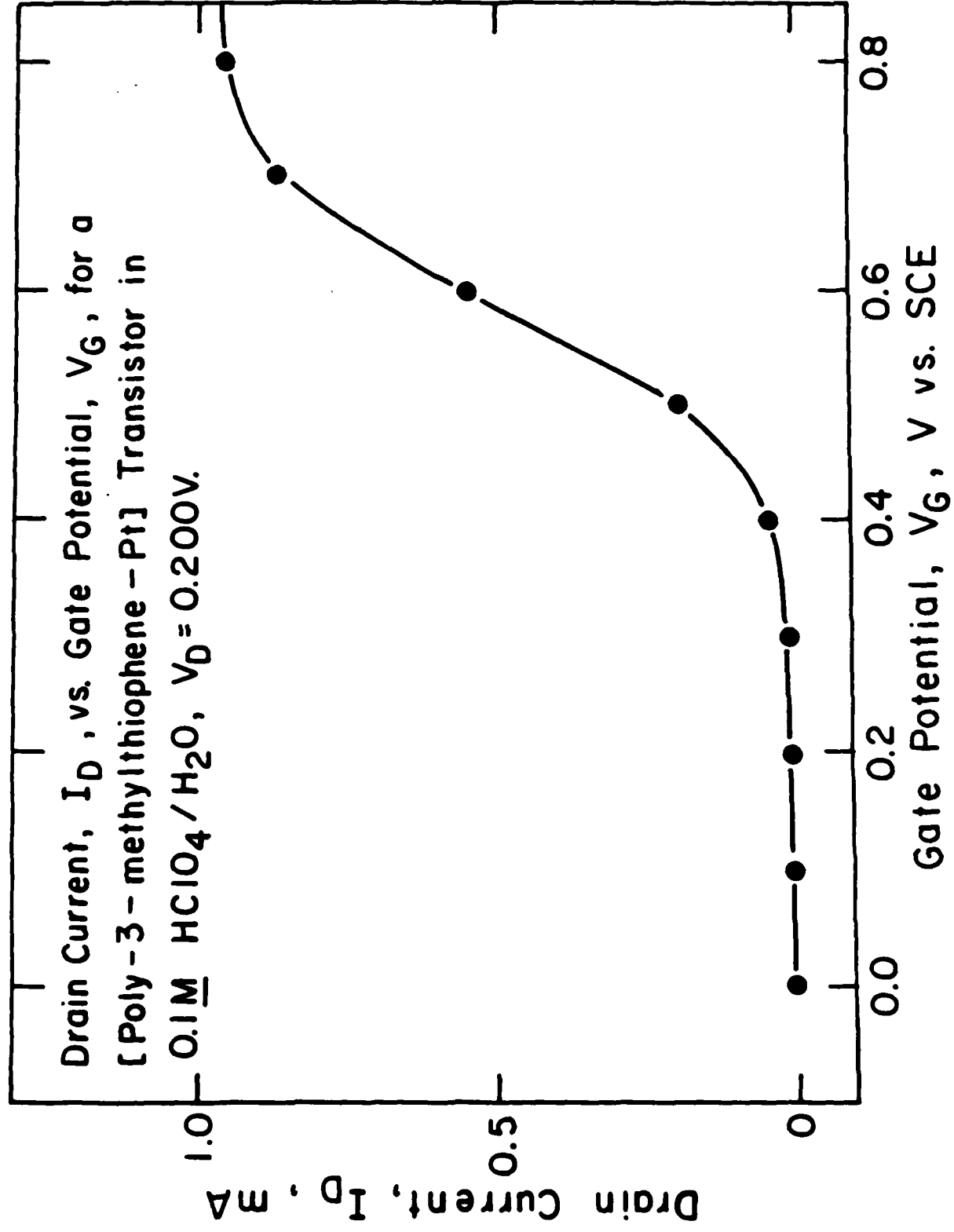
Figure 6.  $I_D$  vs. pH for a [poly(3-methylthiophene)/Pt]-based device, Scheme I, exposed to 1 atm  $O_2$ /0.1 M  $NaClO_4/H_2O$ ,  $V_D = 0.200$  V.

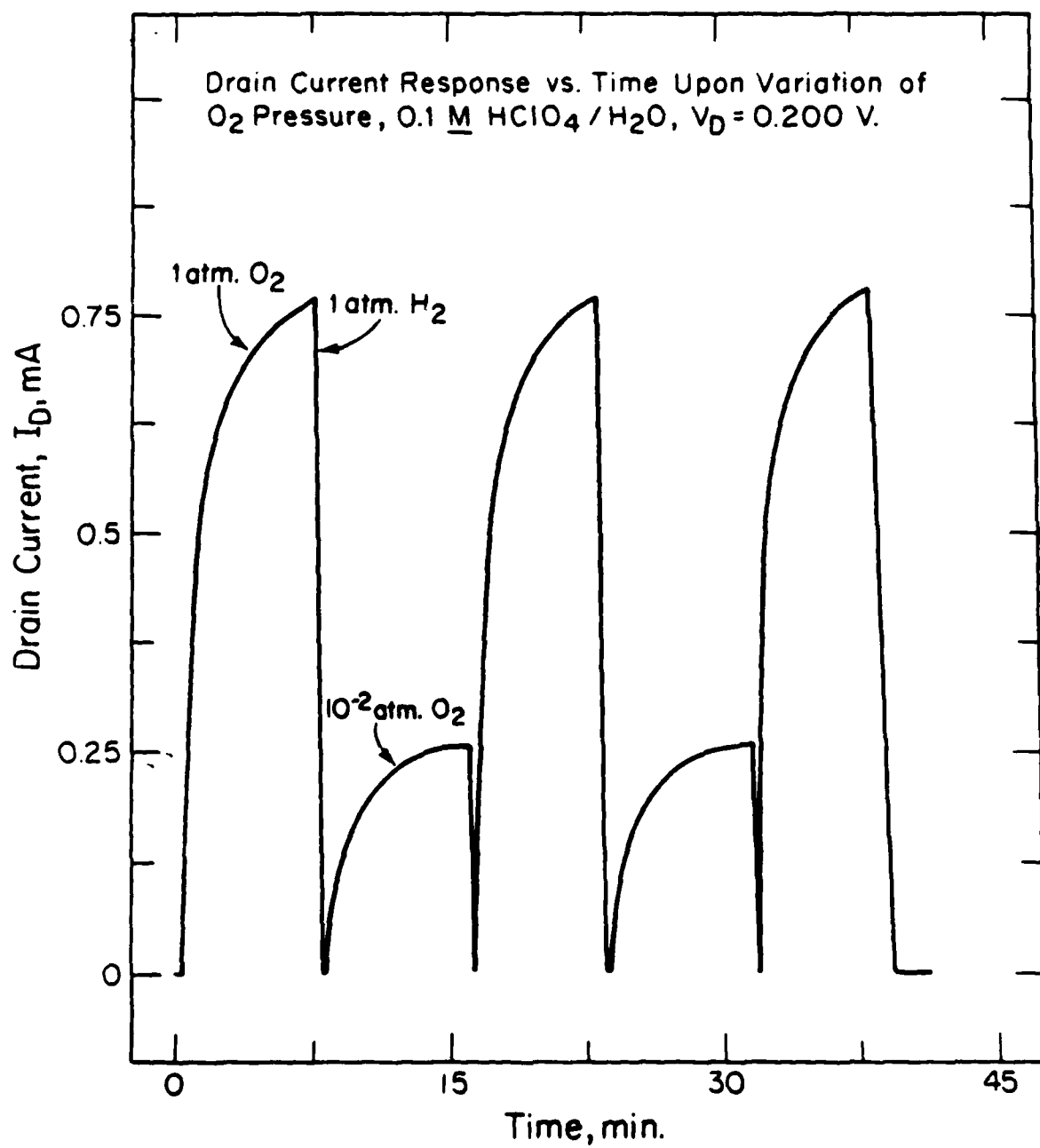
Figure 7.  $I_D$  vs. time for a two terminal [poly(3-methylthiophene)/Pt]-based device upon periodic alternation between pH 5.5 and 6.5 at  $V_D = 0.200$  V.

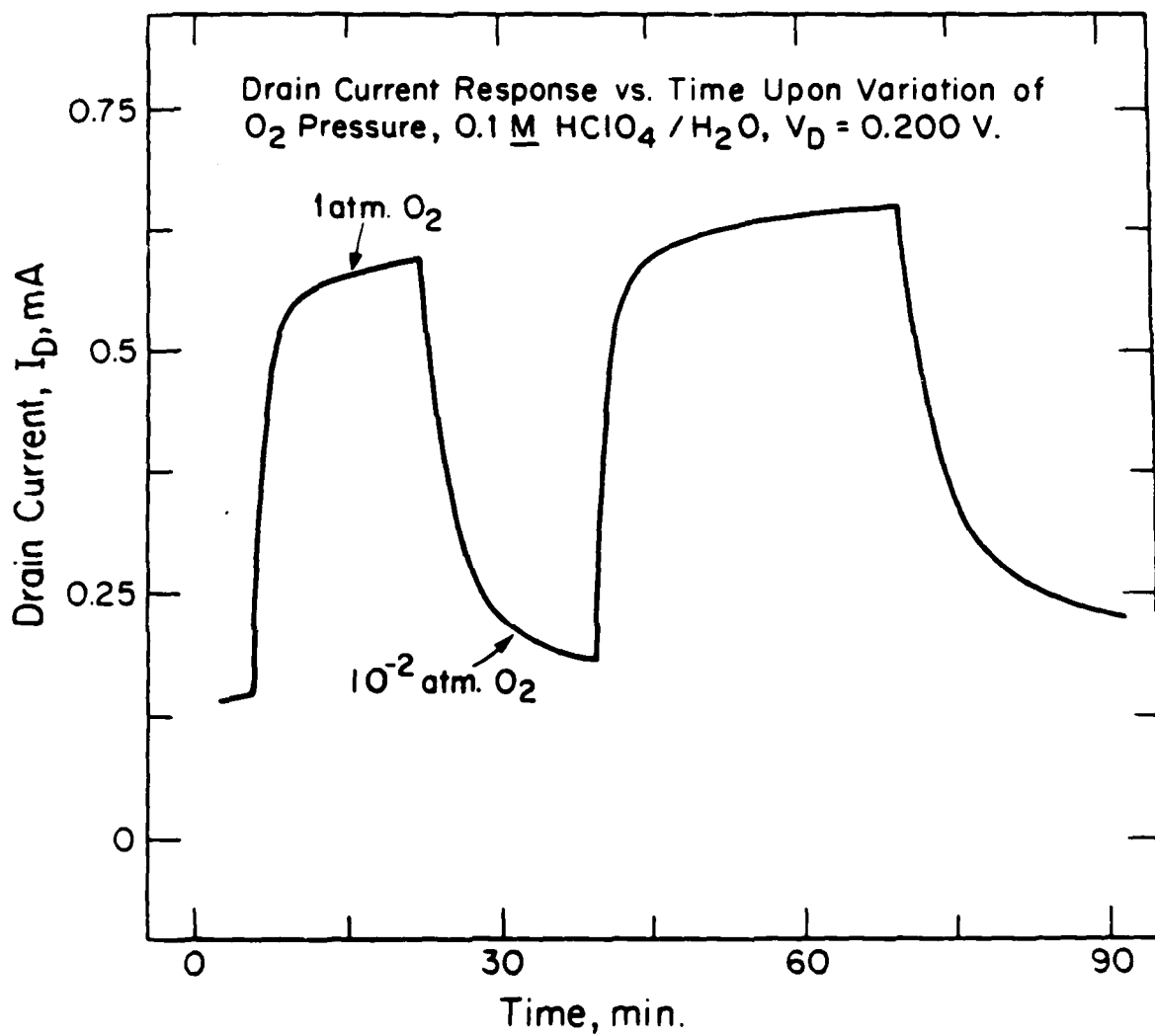
Figure 8.  $I_D$  vs. time for a two terminal [poly(3-methylthiophene)/Pt]-based device upon injection of 1 microliter of 0.1 M  $HClO_4$  into an unbuffered, pH 6.0, 0.1 M  $NaClO_4$  effluent stream at  $V_D = 0.200$  V.

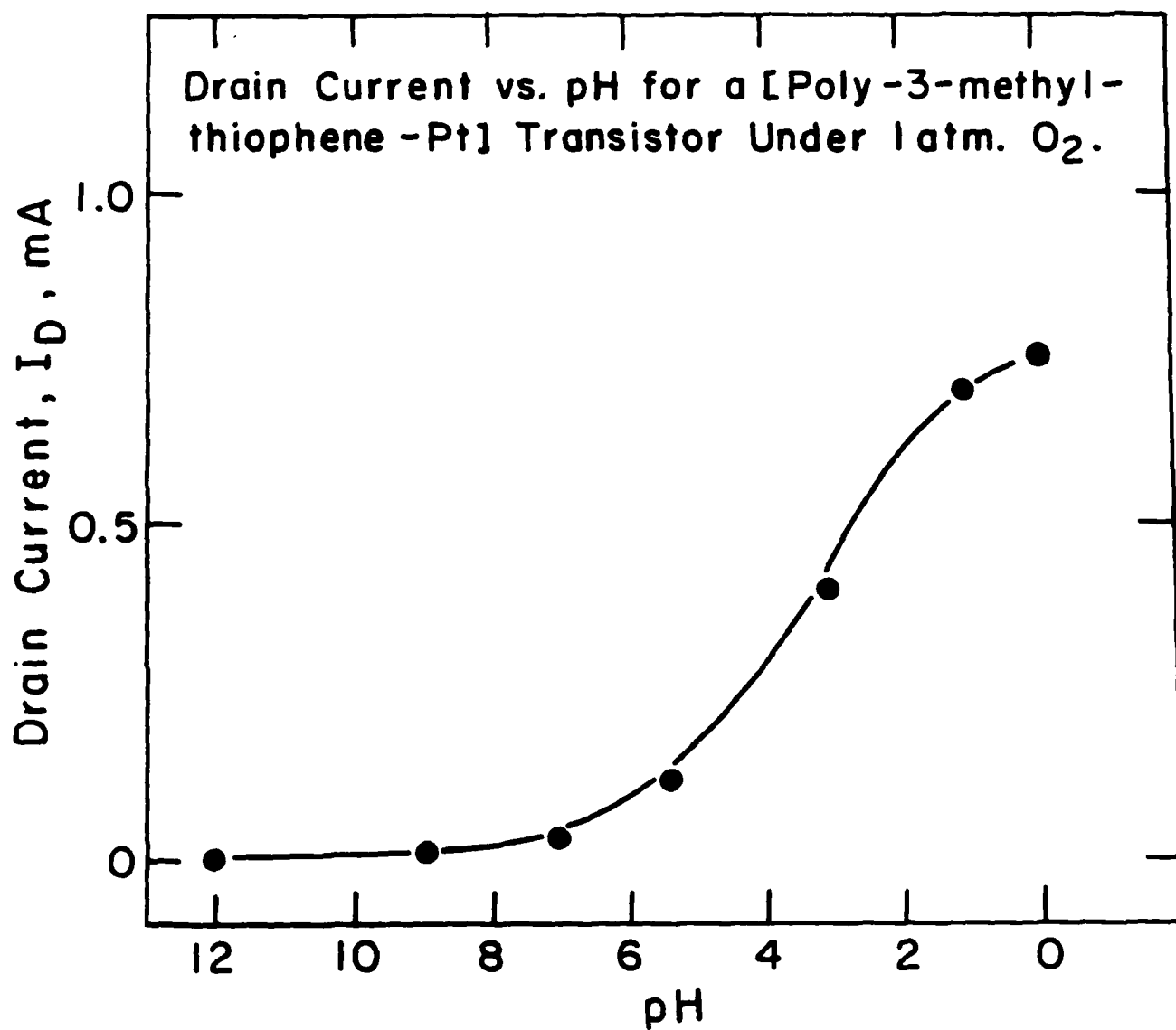




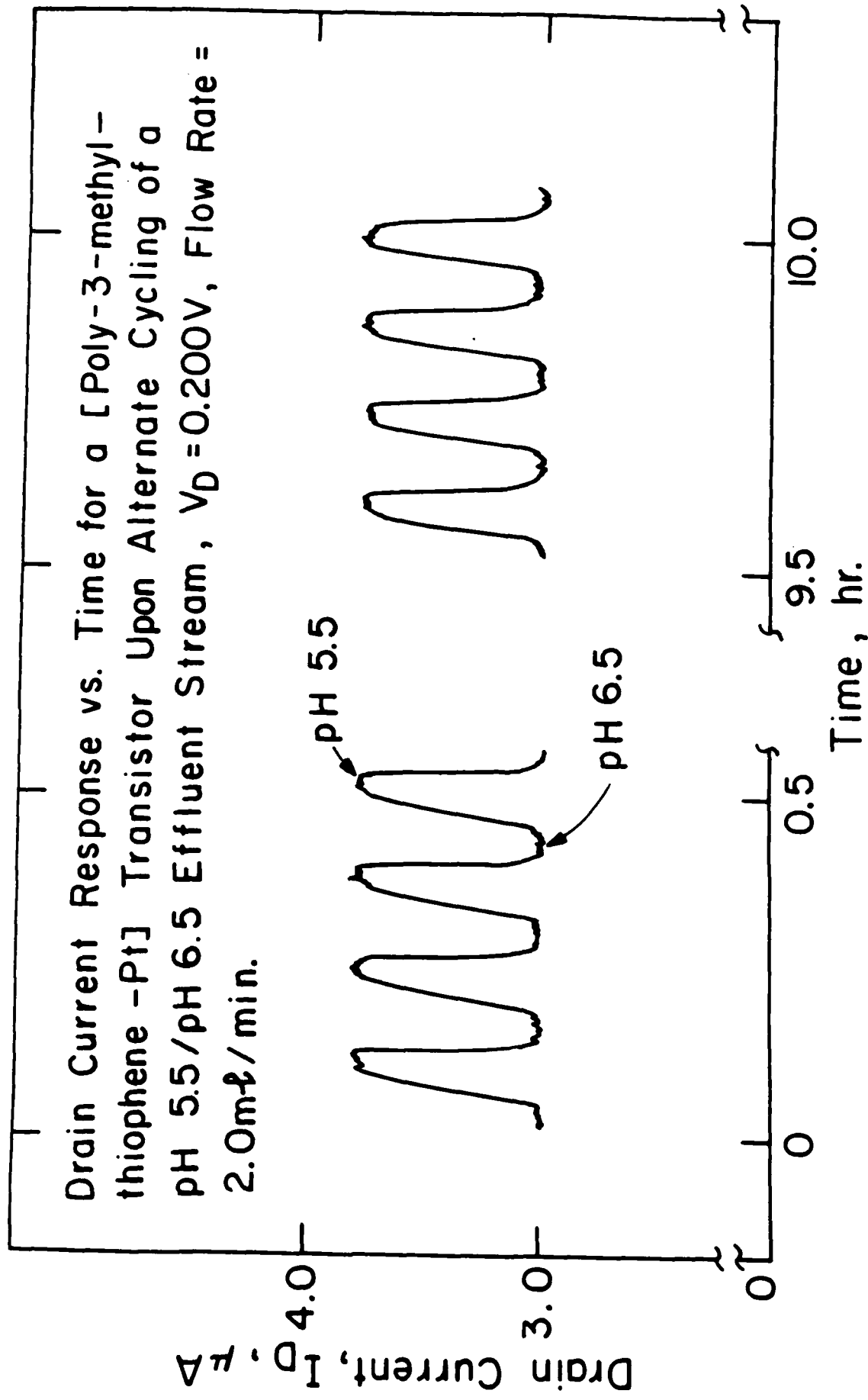


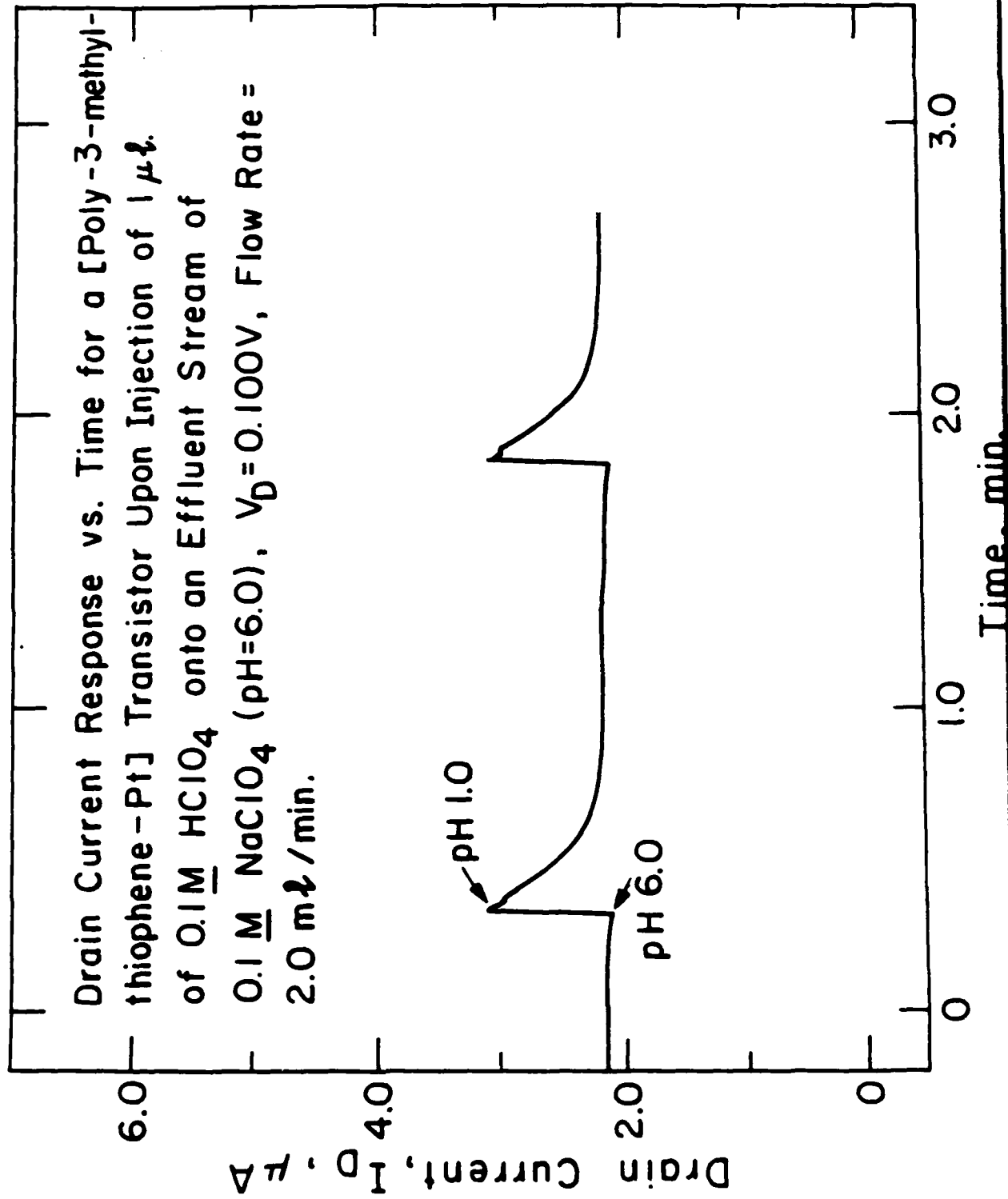












END

10-86

DTIC